Preparation of Large Grained $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ Icosahedral Quasicrystal Directly from the Melt

Yoshihiko Yokoyama, Kenzo Fukaura and Hisakichi Sunada

Faculty of Engineering, Himeji Institute of Technology, Himeji 671-2201, Japan

Various phase diagrams including an icosahedral (i-) phase in Al–Cu–Fe alloy system were examined in order to reveal the composition of the liquid in equilibrium with the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase. The i-phase was formed through the peritectic reaction between the liquid and the primary λ_2 -crystal. Prevention of the peritectic reaction was necessary to produce a single quasicrystal, however, there was a little compositional area of the molten alloy, which can crystallize the i-phase as a primary crystal. In the conventional solidification of $\text{Al}_{60}\text{Cu}_{37}\text{Fe}_3$ alloy, almost primary crystalline particles were classified as i-phase, and the rests were λ_2 -phase. The λ_2 -particles acted as the inhomogeneous crystallization sites of an i-quasicrystal growth. So, several metallurgical treatments were tried to prevent the λ_2 -crystallization. Consequently, we found out an $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$ molten alloy, which can crystallize the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase as a primary crystal at 978 K. The $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$ molten alloy should be treated the preliminary cyclic melting process to prevent the λ_2 -crystallization. And we succeeded to grow up the large grained $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystal directly from the molten alloy.

(Received December 1, 1999; Accepted April 10, 2000)

Keywords: icosahedral quasicrystal, aluminum-copper-iron alloy system, phase diagram, Bridgman method

1. Introduction

A large number of studies have been carried out to discover new stable i- and decagonal (d-) quasicrystals and to clarify atomic structures and physical properties. For about Al–TM system, a lot of stable i- and d-quasicrystals were discovered in Al–Cu–TM (TM = Fe, Ru or Os),^{1,2)} Al–Pd–TM (TM = Mn or Re),^{3,4)} and Al–Co–TM (TM = Cu or Ni)⁵⁾ systems, respectively. The discoveries of these stable quasicrystals have promoted a great progress in the studies of atomic structures and physical properties, since these alloys have superior quasicrystalline structures with neither high density of defects nor phason strains resulting from rapid solidification. In addition, they provided an opportunity to produce a large single quasicrystal. In preparation of a single quasicrystal, clarifying the growth condition of the quasicrystalline solid phase from the melt is the most important process to restrict strains and defects. An ideal quasicrystalline solid growth needs the much time, because the rearrangement of quasicrystalline clusters in the liquid to form the long range aperiodic structure with complicated chemical order. Accordingly, in order to produce a single quasicrystal with superior structural quality, one should produce the single quasicrystal directly from the melt to restrict strains and defects. Actually, in our former works, single i-quasicrystal with a size as large as cm order has been produced directly from the melt in Al–Pd–Mn system with the Bridgman⁶⁾ and the Czochralski method.⁷⁾ Recently, preparation of a single decagonal quasicrystal with cm ordered size has also been produced⁸⁾ directly from the melt in Al–Ni–Co system with the Czochralski method. The systematic investigation for the physical properties change with structural improvement of single quasicrystal by annealing is meaningful and powerful of clarifying the intrinsic properties of ideal quasicrystalline structure.^{9–11)} More recently, we have succeeded to produce the $\text{Al}_{65}\text{Cu}_{15}\text{Co}_{20}$ single d-quasicrystal.¹²⁾ In the Al–Cu–TM alloy system, the liq-

uid phase in equilibrium with the i- or d-quasicrystal is only located in a Cu enriched area. This is quite different from Al–Pd–Mn and Al–Ni–Co systems, because the liquid composition in equilibrium with the i- or d-phase is located in an Al enriched area. A λ_2 -phase with Al_3Fe type intermetallic compound usually crystallizes as a primary crystal even in a Cu enriched compositional area in Al–Cu–Fe alloy system. The λ_2 -phase exhibits the similar structure of λ_1 -phase with Al_3Fe orthorhombic structure, and acts as the primary crystal of the peritectic reaction $L + \lambda_2 \rightarrow \text{I}$. This quasicrystal formation mechanism is also different from Al–Pd–Mn and Al–Ni–Co systems, because the primary crystal of the peritectic reaction is a β -phase with $\text{Al}_{50}(\text{Pd}, \text{Mn})_{50}$ type cubic B2 structure. In Al–Cu–Fe system, the β -phase is only seen in higher temperature, because the λ_2 -phase is formed by the peritectic reaction between the liquid and the β -phases. However, the same formation mechanism of i-phase is also seen in Al–Cu–Ru, Al–Cu–Os and Al–Pd–Re systems. This fact means the superior thermal stability of the λ_2 -phase in Al–Cu–Fe system and also means the difficulty of the i-quasicrystal growth directly from the melt.

The aim of this paper is to reveal the existence of two-phase i- and liquid region, which is contacted to the single liquid phase region. Such a phase diagram means the possibility of i-quasicrystal growth directly from the melt. So, several pseudo binary phase diagrams including an i-phase were examined in this work. On the bases of these diagrams, we tried to grow up a large grained Al–Cu–Fe i-quasicrystal directly from the melt with the Bridgman method.

2. Experimental Procedure

The samples used in the present study on phase diagrams were ternary Al–Cu–Fe alloys in the compositional area from 5 to 45 at%Cu and from 0 to 25 at%Fe. These alloy ingots were prepared by arc-melting in an argon atmosphere. The master alloys were annealed over 48 h at several temperatures

in the two- or three-phase coexist region including a liquid phase in order to obtain an equilibrium state. And then, the sample was quenched quickly to freeze the structure, which can reveal the relation between the solid and the liquid phases. The compositions of several phases in the quenched alloys were determined by electron probe microanalyzer (EPMA). And pseudo-binary cross sections of ternary phase diagram were also investigated by the measuring of solidification reaction temperatures with differential thermal analyzer (DTA). In DTA measurement, the sample was perfectly melted in flowing high-pure Ar atmosphere for 3.6 ks at the temperature about 100 K higher than the liquidus line temperature, and the solidification processes was examined with slow cooling rate about 0.033 K/s. A structural identification was made by X-ray diffractometry and back scattering X-ray Laue diffractometry (Cu K_α), and the quenched structures and the solidified morphologies were examined by scanning electron microscope (SEM).

3. Results and Discussion

Almost previous reports till 1984 about an Al–Cu–Fe ternary phase diagram pointed out the difficulty of the i-phase growth directly from the melt. For example, the pseudo-binary phase diagram of $\text{Al}_{97-X}\text{Cu}_X\text{Fe}_3$ ($X = 0\text{--}40\text{ at}\%$) by Phillips¹³⁾ suggested that the preparation of i-single quasicrystal directly from the melt was impossible, whereas an i-phase was not identified as an individual stable phase. However, some recent reports¹⁴⁾ described about the existence of two-phase i- and liquid region, which implied the possibility of an i-crystallization as a primary crystal. Accordingly, the phase diagrams involving an i-phase were examined in order to clarify the existence of two-phase i- and liquid region. Figure 1 shows the constitutional diagram of Al–Cu–Fe alloy system,¹⁵⁾ and also indicates compositional lines of cross sections (dotted lines) and a compositional area of liquidus surface diagram (shadowed area) in this study. Pseudo-binary phase diagram along the $\text{Al}_{65}\text{Cu}_{35-X}\text{Fe}_X$ compositional line was examined as shown in Fig. 2. This figure means that the formation temperature of i-phase is much more below than that of λ_2 -phase. From this diagram, the formation mechanism of i-phase is also recognized as the peritectic reaction of $\text{L} + \lambda_2 \rightarrow \text{I}$ (I: i-phase), which is different from the stable Al–Pd–Mn i-quasicrystal in our former work,⁴⁾ as far as the primary crystal of the peritectic reaction is not a β -phase. Noteworthy point in this figure, there is no boundary between the liquid and the two-phase i- and liquid regions. The formation mechanism of the i-phase was also examined by the structural observation of water quenched $\text{Al}_{65}\text{Cu}_{32}\text{Fe}_3$ samples after annealed at 1123, 1023 and 923 K as shown in Fig. 3. This figure (b) shows some crystallized λ_2 -particles with a prism rod shape. And the peritectic reaction between the liquid and the λ_2 -phases is occurred to produce the i-phase in this figure (c). The solidification morphologies of the i-phase is seems a dendritic shape, because the individual pentagonal shapes are observed on lines with a geometrical symmetry. So, the dendritic growth of the i-phase indicates that the formation mechanism of the i-phase is not only the peritectic reaction ($\text{L} + \lambda_2 \rightarrow \text{I}$) but the incongruent solidifi-

Al–Cu–Fe constitutional diagram

Fig. 1 Constitutional diagram of Al–Cu–Fe ternary alloy system.¹⁵⁾

Fig. 2 Pseudo binary phase diagram along the $\text{Al}_{65}\text{Cu}_{35-X}\text{Fe}_X$ ($X = 0$ to 20 at%) compositional line.

cation ($\text{L} \rightarrow \text{I}$), because the second arms of the i-dendrite contain no primary λ_2 -crystal. This fact brings out the optimistic expectation that the two-phase i and liquid region is contacted to the single liquid region at somewhere in Al–Cu–Fe ternary alloy system. Next, Fig. 4 shows pseudo-binary phase diagrams along $\text{Al}_{98.5-X}\text{Cu}_X\text{Fe}_{1.5}$, $\text{Al}_{97-X}\text{Cu}_X\text{Fe}_3$ and $\text{Al}_{95-X}\text{Cu}_X\text{Fe}_5$ ($X = 0\text{--}40\text{ at}\%$) compositional lines to confirm that the two-phase i- and liquid region is contacted to the liquid phase. As the result, we found out the two-phase i- and liquid region, which was contacted to the single liquid region in narrow compositional area around $\text{Al}_{60}\text{Cu}_{37}\text{Fe}_3$ as shown in Fig. 4(b). However, the two-phase i- and liquid region frequently contained a small amount of λ_2 -phase, because the i-formation peritectic reaction finished hardly even in slow cooling solidification. Figure 5 shows water quenched structures of $\text{Al}_{60}\text{Cu}_{37}\text{Fe}_3$ samples after annealed at 1073 K (a), (b) and 1023 K (c), (d). In this figure, analyzed elements

Fig. 3 SEM images of water quenched samples from 1123, 1023 and 923 K, and analyzed composition of several phases with EPMA.

of samples were collected Al, Cu, Fe and Si, because the sample was reacted to a little of quartz tube by the homogenizing anneal treatment in the melt state. At 1073 K, just below the melting temperature, the i-phase grew larger than the λ_2 -phase (Figs. 5(a), (b)). And at 1023 K, the i-particle grew much larger one, besides crystallized λ_2 -phase changes to the smaller one by the peritectic reaction of i-formation (Figs. 5(a), (b)). This fact means the all of λ_2 -particles act as the inhomogeneous crystallization site of i-phase, however, almost i-particles form directly from the melt in $Al_{60}Cu_{37}Fe_3$ alloy. Problems of the λ_2 -inclusion are summarized as follows; (1) the compositional and the temperature range of the liquid with primary i-crystallization is too narrow to prevent perfectly the λ_2 -crystallization, (2) primary crystallized λ_2 -particles promote the inhomogeneous i-crystallization by the peritectic reaction. So, prevention of the λ_2 -crystallization is essential procedure to produce the large grained i-phase directly from the melt. Consequently, to reveal the compositional area of the liquid phase which can crystallize an i-phase as a primary crystal, we produced the partial liquidus surface (solid lines) and the i-formation temperature diagram (dotted lines) as shown in Fig. 6. The compositional area of the liquid phase with a primary crystal as only an i-phase is located

Fig. 4 Cross sections of ternary Al-Cu-Fe alloy system along $Al_{98.5-X}Cu_XFe_{1.5}$ (X = 30 to 40 at%) (a), $Al_{97-X}Cu_XFe_3$ (X = 30 to 40 at%) (b) and $Al_{95-X}Cu_XFe_5$ (X = 30 to 40 at%) (c) compositional lines, respectively.

Fig. 5 SEM images of water quenched $\text{Al}_{60}\text{Cu}_{37}\text{Fe}_3$ samples from 1073 K (a), (b) and 1023 K (c), (d), and analyzed compositions of the liquid phase and the solid i- and λ_2 -phase by EPMA.

Fig. 6 Diagram of liquidus surface (solid lines) and formation temperature of i-phase (dotted lines) in Al-Cu-Fe ternary alloy system.

in narrow area from 37.5 to 38 at% Cu and from 3 to 3.3 at% Fe (shadowed area in Fig. 6). It is too narrow to control the liquid composition with conventional solidification process, so we tried to treat some special metallurgical treatments for prevention of the λ_2 -crystallization. Via the trial and error,

ultimately, we found out the effective element of Si to delay the λ_2 -crystallization. Adding a Si element condensed preferentially to the λ_2 -phase as shown in Fig. 5, and the formation temperature of the λ_2 -phase should be below than that of the i-phase. Confirmation of the i-formation directly from the Al-Cu-Fe-Si quaternary molten alloy and determination of optimum Si concentration were done by DTA thermal analysis and structural observation. As the result, Fig. 7 shows the DTA curves of $\text{Al}_{60-X}\text{Cu}_{37}\text{Fe}_3\text{Si}_X$ ($X = 0, 1$ and 3 at%) alloys with slow cooling rate 0.067 K/s, and also shows the several SEM images of quenched samples from the temperatures just below the first peaks in order to identify the primary crystal. In the $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$ alloy, only an $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase crystallized directly from the melt. Since the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase is characterized by the superior thermal phase stability, the alloy composition was chosen for the large grained i-quasicrystal preparation in this study. The adding 1 at% Si is effective for the prevention of λ_2 -crystallization. However, the excess Si element causes the change of primary crystal from i-phase to cubic approximant phase. For about $\text{Al}_{57}\text{Cu}_{37}\text{Fe}_3\text{Si}_3$ alloy, a cubic approximant phase with 1/1 type was observed mainly, and examined the composition of the phase was about $\text{Al}_{57}\text{Cu}_{24}\text{Fe}_{12}\text{Si}_7$. Consequently, we tried to produce the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystal directly from the melt with the Bridgman method using the $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$

Fig. 7 DTA curves of $\text{Al}_{60-x}\text{Cu}_{37}\text{Fe}_3\text{Si}_x$ ($x = 0, 1$ and $3\text{at}\%$) alloys with slow cooling rate 0.067 K/s , and SEM images of the quenched three samples from the temperatures just below the first peaks.

master alloy. Before Bridgman process, preliminary procedure should be done for the $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$ master alloy to prevent the λ_2 -crystallization. The preliminary process is repeat of melting and solidification by the cyclic heating with temperature change between upside and downside of the liquidus line over 10 times. The effect of this process is guessed that the adding Si element concentrates to the λ_2 -embryo and decrease the melting temperature of λ_2 -phase. A schematic illustration of the Bridgman method is shown in Fig. 8(a),

and this figure also shows outer appearance of the sample produced with the Bridgman method (b). A back scattering X-ray Laue diffraction pattern taken from the cross section of A-A plane with an incident beam along the growth direction is shown in Fig. 8(c). The preferential growth direction of i-quasicrystal is estimated the 3-fold direction, because the solidified morphology of an i-quasicrystalline particle is usually seen a dodecahedron shape. In this figure (b), individual dodecahedron morphology shapes are seen in several part of

Fig. 8 Schematic illustration of the Bridgman method (a), outer appearance of the sample produced with the Bridgman method (b) and back scattering X-ray Laue diffraction pattern (c) taken from the cross section of A-A plane with an incident beam along the growth direction.

Fig. 9 Solidification morphology of the single $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystalline particle produced with the Bridgman method.

the sample with arrow head marks. Figure 9 shows the magnified SEM image of one of i-quasicrystalline particles on the free solidified surface of the sample, and analyzed mean composition is about $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$. The i-particles surrounded by the chill structure, so the i-quasicrystal was formed directly from the melt. Consequently, we are planning the preparation of a large single $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystal with the Czochralski method. In the Czochralski method, the seed will be prepared by the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-single sample, which was

produced with the Bridgman method in this study. We will report about the investigation in this journal soon.

4. Summary

Cross sections of the ternary Al–Cu–Fe phase diagram were examined with the aim of compositional area determination of the liquid, which can crystallize the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase as a primary crystal. On the basis of the information, the preparation of the large grained $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystal was tried with the Bridgman method. The results obtained are summarized as follows:

(1) The i-phase was formed through the peritectic reaction between the liquid and the λ_2 -phases. In order to produce the i-quasicrystal directly from the melt, we found out the much narrow compositional area (37.5 ~ 38 at%Cu, 3 ~ 3.3 at%Fe) of the liquid, which can crystallize an i-phase as a primary crystal.

(2) In order to prevent the λ_2 -crystallization, several metallurgical treatments were tried. Ultimately, we found out the $\text{Al}_{59}\text{Cu}_{37}\text{Fe}_3\text{Si}_1$ molten alloy, which can crystallize the $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-phase as a primary crystal at 978 K. Before the solidification, the molten alloy should be done the preliminary cyclic melting process to prevent the λ_2 -crystallization.

(3) We succeeded to produce the large grained $\text{Al}_{64}\text{Cu}_{23}\text{Fe}_{13}$ i-quasicrystal directly from the melt with the Bridgman method.

REFERENCES

- 1) A. P. Tsai, A. Inoue and T. Masumoto: Jpn. J. Appl. Phys., **26** (1987), L1505–1507.
- 2) A. P. Tsai, A. Inoue and T. Masumoto: Jpn. J. Appl. Phys., **27** (1988), L1587–1590.
- 3) A. P. Tsai, Y. Yokoyama, A. Inoue and T. Masumoto: Jpn. J. Appl. Phys., **29** (1990), L1161–1164.
- 4) A. P. Tsai, Y. Yokoyama, A. Inoue and T. Masumoto: Mater. Trans., JIM, **31** (1990), 98–103.
- 5) A. P. Tsai, A. Inoue and T. Masumoto: Jpn. J. Appl. Phys., **30** (1989), 463–473.
- 6) Y. Yokoyama, A. P. Tsai, A. Inoue and T. Masumoto: Mater. Trans., JIM, **32** (1991), 1089–1097.
- 7) Y. Yokoyama, T. Miura, A. P. Tsai, A. Inoue and T. Masumoto: Mater. Trans., JIM, **33** (1992), 97–101.
- 8) Y. Yokoyama, R. Note, S. Kimura, A. Inoue, K. Fukaura and H. Sunada: Mater. Trans., JIM, **38** (1997), 943–949.
- 9) Y. Yokoyama, Y. Yamada, K. Fukaura, H. Sunada, R. Note, A. Inoue, K. Sugiyama and K. Hiraga: Jpn. J. Appl. Phys., **39** (1999), 1495–1499.
- 10) Y. Yamada, Y. Yokoyama, K. Matono, K. Fukaura and H. Sunada: Jpn. J. Appl. Phys., **38** (1999), 52–55.
- 11) K. Soda, U. Mizutani, Y. Yokoyama, R. Note, A. Inoue and M. Fujiwara: *Proc. of ICQ6 World Scientific Publishing Co. Ltd.*, Singapore, (1997), 676–679.
- 12) Y. Yokoyama, R. Note, A. Yamaguchi, A. Inoue, K. Fukaura and H. Sunada: Mater. Trans., JIM, **40** (1999), 123–131.
- 13) H. W. L. Phillips: J. Inst. Metals, **82** (1953), 197–212.
- 14) F. W. Gayle, A. J. Shapiro, F. S. Bincaniello and W. J. Boettinger: Met. Trans. A, **23** (1992), 2409–2413.
- 15) J. A. Bradley and H. J. Goldschmidt: J. Inst. Metals, **73** (1938), 403–418.